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RECENT RESEARCH ON CRYOGENIC DEUTERIUM-TRITIUM

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ABSTRACT

We present recent cryogenic D-T data measured in our laboratory. By infrared spectroscopy, we find chemical reaction 1/e-times for D_2-T_2 of 54h for the 23 K liquid and 88h for the 18.6 K solid. Nuclear magnetic resonance shows that the rotational J=1→0 1/e-times in solid T_2 shortens as the temperature falls. At 9 K, it is only 60 minutes. A first solid thermal conductivity value of 0.05 W/m-K in 10 K T_2 shows that heat removal will be slow in the solid. Finally, D-T gas conducts electricity as well as the liquid; both are soft dielectrics with conductivities on the order of 10^{-7} $(\Omega\text{-m})^{-1}$.

INTRODUCTION

Solid deuterium-tritium (D-T) may be used as a future hydrogen fusion fuel. To aid in engineering this material, we are measuring various physical and chemical properties of cryogenic D-T in the solid, liquid, and gas phases. We are concentrating on those properties most likely to be affected by the tritium radioactivity.

D-T REACTION RATE

Of considerable interest is the reaction rate of D_2 and T_2 to form the three-component mixture, D_2-DT-T_2. At room temperature, this reaction takes place with an exponential 1/e-time on the order of tens of minutes, depending on the gas pressure and the vessel wall conditions.[1] We are measuring this reaction in the liquid and solid at about 20 K. The 1/e-times are on the order of tens of hours.

We are using the technique of collision-induced infrared absorption. Hydrogen molecules are diatomic; H_2, D_2, and T_2 are totally symmetric and do not possess permanent electric dipole moments. The mixed isotopes - HD[2], HT, and DT possess such small permanent moments that the usual allowed infrared lines (of the sort that we see in HF or CO_2) do not appear. If the hydrogen molecules approach one another closely, they induce weak effects by means of the transient electric dipole moment and the permanent electric quadrupole moment. This produces an infrared absorption about 10^{-5} times as strong as that of an allowed transition.

We have taken the first infrared spectra of liquid and solid D-T.[3] A typical liquid sample is shown in Figure 1. From left to right are the spectral regions belonging to T_2, DT, and D_2. Each hydrogen has a different mass and therefore vibrates at a different frequency. The pure vibrational lines (called $Q_1(0,1)$)[4] with quantum number v=0→1) for T_2, DT, and D_2 occur at 2458, 2736, and 2986 cm^{-1}. The other lines represent the vibrational transition plus molecular rotational or crystal vibrational transitions. The best peaks to use for quantitative analysis of D_2-T_2 mixtures with a small amount of DT are the "double transitions" shown in Fig. 1. (These are called the $Q_1(0,1)$ XY + $S_0(0)$ D_2 lines,[4] where XY represents T_2, DT, and D_2). The first molecule (XY) undergoes only a v=0→1 excitation, but the second molecule (D_2) gains rotational energy (v=0, rotational quantum number J=0→2). These are the largest peaks in the spectrum, and they measure the relative amounts of the first molecule (XY) in the double transition. We have measured the peak heights, and connected them for the exponential aborption of the infrared beam in the sample. We also correct for the sensitivity difference due to mass: T_2 lines are 20% smaller than D_2 lines. The three peaks used for measuring T_2, DT, and D_2 mole fractions occur at 2636, 2916, and 3164 cm^{-1}.

It is clear that we may determine the D_2-T_2 chemical reation rate by observing the changes in the heights of three selected peaks. The use of peak heights is approximate, and better numbers will be derived from a peak-unfolding and area-measuring computer program now under construction by J. Hunt.[5] Our initial data is shown in Fig. 2. It is consistent with an exponential fit. The 1/e-times (time to 0.368 of the original signal) are 54h for the 23 K liquid and 88h for the 18.6 K solid. The chemical reaction

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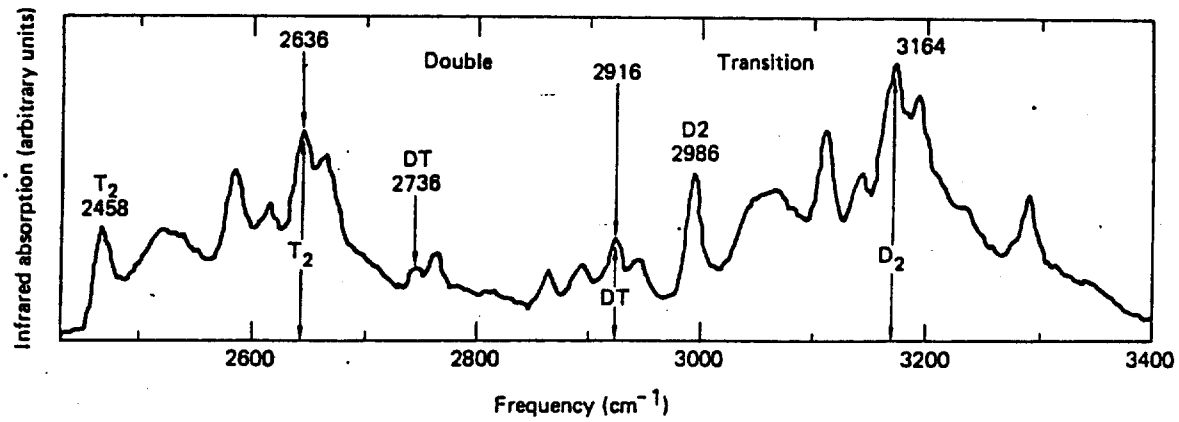

Fig. 1. A typical D_2-T_2 collision-induced infrared spectrum: the liquid at 21 K. DT is forming by chemical reaction in the center of the spectrum. The three "double transition" lines used for quantitative analysis are indicated. The other marked lines are the pure vibrational transitions that mark the start of each isotope's spectrum.

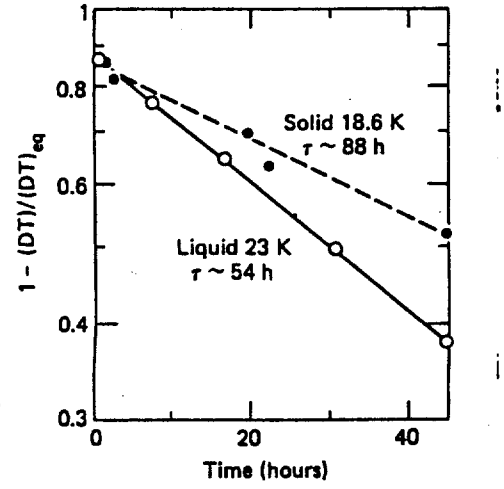

Fig. 2. Reaction of D_2-T_2 to form DT as measured in the solid and liquid by infrared spectroscopy. The reactions are exponential within error.

is slow.

J=1→0 ROTATIONAL TRANSITION RATES

When HD, HT, or DT are rapidly cooled, the molecular rotational energy levels quickly de-excite, as expected, to the ground (J=0) state. Because of quantum symmetry, this does not happen for H_2, D_2, and T_2. Instead, these fall to the J=1 state and only slowly make the final jump (the "ortho-para" effect). The amounts of energy in the J=1→0 transition are 715 and 479 J/mole for D_2 and T_2. But this is small compared to the 0.977 W/mole T heat of tritium's radioactive decay.[6] The metastable rotational phenomenon is important because it appears in various techniques of measurement, e.g., the infrared spectra. It is constantly in the way, and sometimes, it even affects physical properties to a considerable degree (e.g., solid thermal conductivity).

With J. Gaines of Ohio State University, we have studied the J=1→0 rotational reaction time in solid T_2 using pulsed nuclear magnetic resonance (n.m.r.).[7] A pulse of radiofrequency energy excites the nuclei, and they ring at the same frequency. The height of the ringing at the instant the exciting pulse turns off is a direct measure of the number of excited nuclei. J=0 T_2 gives no n.m.r. signal because the two nuclear moments are alligned in opposition to each other. J=1 T_2 gives a signal because the nuclear moments reinforce each other. We can measure the reaction time by the decline of the J=1 T_2 n.m.r. signal.

The rotational 1/e-times in T_2 are shown in Fig. 3. The solid data from 8 to 13 K are exponential; from 18 K to the 22 K liquid point, the decay may not be exponential. We note that the reaction times become faster as the temperature falls -- the opposite of what we expect in most reactions. The cause is the build-up of frozen-in radiation-damage products as the temperature decreases. The same trend with free atoms is seen in electron-irradiated H_2[8]; atoms may be catalyzing the J=1→0 transition in solid T_2. The comparable time in pure H_2 is on the order of days.[9]

SOLID THERMAL CONDUCTIVITY

As mentioned above, tritium decay furnishes an astonishing amount of heat. How to get rid of this heat is the first order of business in a cryogenic system. This makes the solid thermal conductivity and diffusivity important properties for the engineering of solid D-T.

The solid thermal conductivity is the most sensitive indicator of hydrogen crystal quality. Fig. 4 shows data for H_2 and HD.[10-12] Note

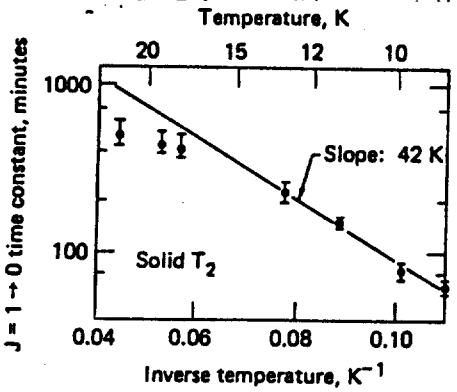

Fig. 3. The J=1→0 rotational reaction rate in solid T_2. Note that the rate increases as the temperature falls. Atomic tritium may be the catalyst.

now it extends over six orders of magnitude--from a value like room temperature copper to that of air. The low temperature thermal conductivity increases with temperature because more phonons (quantum units of crystal heat) are formed. At higher temperatures, they collide with one another, and the flow of heat is impeded. For this reason, the peak occurs at 4 K.

The dotted line in Fig. 4 would be the thermal conductivity of a perfect H_2 crystal, in which a phonon bounces back and forth off the inside faces. No one has ever prepared a crystal this good, but efforts continue.[13] The J=0 H_2 line is the best crystal so far. The normal (n)-H_2 curve lies far below. The phonons are scattered and impeded by the 75% of J=1 H_2 molecules. This illustrates the extreme sensitivity of the thermal conductivity, for the crystal would appear to be optically perfect.

Fig. 4 contains one very crude 10 K solid T_2 point of about 0.05 W/m-K.[14] We obtained it from the J=1 concentration as seen by infrared spectroscopy for a T_2 sample that had equilibrated after 8h. The average sample temperature was hotter than the wall temperature, and we estimated an enormous 8 K/cm temperature gradient in the solid T_2. Frozen hydrogen shrinks as it cools and pulls away from the vessel walls. Thus, our thermal conductivity value quite probably includes a gas space.

There is every reason to suspect that the thermal conductivity of D-T will be low. The radiation damage will produce defects off which phonons will scatter. Eventually, the radiation damage may begin to crack the crystal. Worse yet may be the effects of mixing isotopes. A mixture under its saturation pressure resists the formation of large crystals. Such grain boundaries will surely hamper heat flow. The position of the T_2 point in Fig. 4 may not be so bad after all.

One cure for these problems is pressure. A

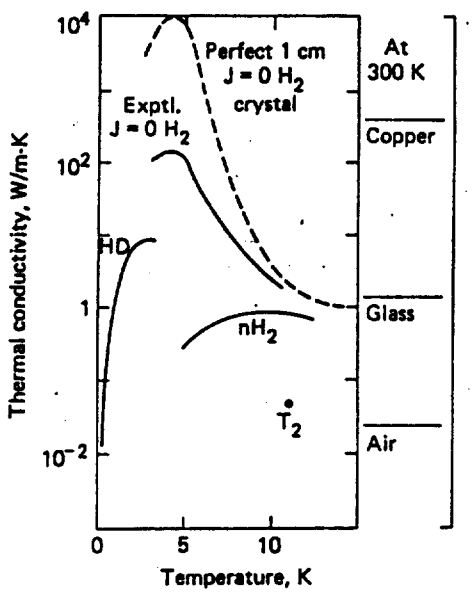

Fig. 4. Thermal conductivity of solid H_2 and HD plus our initial T_2 point. The range of values is six orders of magnitude.

few atmospheres is enough to induce H_2 and D_2 to form clear crystals.[15] To absolutely insure that H_2 fits snugly against the vessels walls at 4 K may require about 50 atmospheres.[16] For D-T, it will be more like 120 atm.[17] The data of Fig. 4 was not measured under pressure.

We are presently constructing a 200-atm thermal conductivity cell. The D-T sample will have the configuration of a tube heater, and it will raise the temperature of the sensor inside it.

ELECTRICAL PROPERTIES

Of all properties that could be sensitive to radiation, electrical conductivity must surely head the list. The 5.6 kev beta particle from the tritium decay loses its energy in roughly 15 ev increments. From every three of these energy losses, one ion and electron are formed.[18]

Pure liquid H_2 is one of the hardest insulators imaginable, with an electrical conductivity of about 10^{-17} $(\Omega\text{-m})^{-1}$.[19] Our 20-26 K data for T_2 is shown in Fig. 5.[20-21] The gas conductivity increases with density and is beginning to saturate at 600 mole/m^3. Both have conductivities in the range 10^{-7} $(\Omega\text{-m})^{-1}$. The tritium has made them into soft dielectrics.

Above 200 mole/m^3, the gas has a higher conductivity than the liquid. The saturated vapor above liquid D-T will be more conductive. Any charge applied to the liquid should leak into the vapor.

The difference between the liquid and the gas

is illustrated by our dielectric constant measurements at 1592 Hz and 2830 V/m. Liquid T_2 has 4 X 10^{10} electric charges/mole, of which 25 to 40% may be electrons. The ion yield is only about 10^{-3} ions pairs/100 e.v. The gas shows about 10^{12} static electric charges/mole, regardless of density. Less than 2% of the charges are probably electrons, and the ion yield is 0.15 - 0.5 ions pairs/100 ev.

It is clear that charge production is more efficient in the gas than in the liquid. In the gas, ions and electrons are further apart and less likely to recombine. In both cases, however, virtually all the current is carried by the high mobility electrons. The ions are about 2000 times slower. They register as static charges in the dielectric constant, but they have no appreciable effect on the electrical conductivity. Electrons may react to form tritide ions and possibly even larger species.[22] This is why the percent of electrons is less than 50%.

Upon freezing, the solid pulls away from the walls and electrical contact is lost. Overpressures of 1 atm do not help. We are presently building a 200 atm electrical conductivity cell to attack this problem.

CONCLUSIONS

Our goal is to accumulate enough data on cryogenic D-T to allow fusion engineers to feel comfortable with this potential fuel. To this end, we are working on D_2-T_2 chemical and rotational kinetics, solid thermal conductivity, and electrical properties.

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4. The notation Q and S refers to a rotational transition of $\Delta J=0$ and 2, respectively. A subscript one or zero indicates the value of the vibrational quantum number change, Δv. The number in parentheses indicates the initial rotational quantum number J of the absorbing molecule.

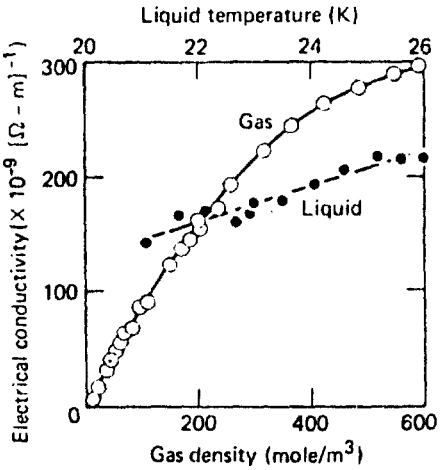

Fig. 5. Electrical conductivity of gaseous and liquid T_2. Above 200 mole/m^3, the gas is a better conductor.

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